Formation Mechanisms of Gold-Zinc Oxide Hexagonal Nanopyramids by Heterogeneous Nucleation using Microwave Synthesis

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Supporting Information

Experimental

Chemicals and Materials

Gold particles were prepared by microwaving a mixture of $HAuCl_4$ (Aldrich, 30 wt % in dilute HCL, 99.99%), oleic acid (Aldrich, technical grade, 90%) and oleylamine (Aldrich) in an 8" test tube until a red color appears, approximately 40 seconds. A 1:1 ratio of oleic acid to oleylamine was used to create spherical particles.

Preparation of the ZnO hexagonal pyramids required 0.09 g anhydrous zinc acetate (Aldrich, 99.99%) to be dissolved in a mixture of 1 mL oleic acid and 4 mL oleylamine. The reaction mixture was heated in a hot oil bath with stirring to 120 °C, and the temperature was maintained for 1 hour. The reaction mixture was immediately removed from the oil bath and microwaved at full power for 15 minutes.

Two methods were used for the preparation of Au-ZnO nanoparticles. In both methods, anhydrous zinc acetate (Aldrich, 99.99%) was dissolved in a mixture of oleic acid and oleylamine in an 8" test tube. The reaction mixture was heated in a hot oil bath with stirring to 120 °C, and temperature was maintained for 1 hour. In one method, gold particles, as prepared above, were added to the zinc reaction mixture and stirred vigorously until homogeneous in color. In a typical reaction, 0.5 mL of Au seed solution was added to 4 mL of zinc precursor solution, unless otherwise specified. Then, the solution was microwaved. Microwaving time was varied between 8 and 15 minutes. In the second method, $HAuCl_4$ was added to the zinc reaction mixture. The solution was stirred until it became homogeneous in color and then microwaved. Following the microwave reaction, the precipitate was separated from the liquid phase by centrifugation, 12,857 *g* for 10 minutes, and dried at 60 °C overnight. No additional washing was performed.

For all the syntheses described here, a conventional microwave oven, Emerson MW8119SBM, operating at 600 – 1000 W was used. In most cases, the reaction mixture was mircrowaved in 30 second cycles (on for 10 s, off and stirring for 20 s) for reaction times that varied from 10 s to several minutes.

Table 1. Experimental parameters for the two-step synthesis of Au-ZnO nanopyramids by heterogeneous nucleation on preformed Au nanoparticles.

Ratio OAc:OAm	Au	Zn acetate (M)	OAC (mL)	OAM (mL)
1:2	0.5 mL seeds	0.05	1.4	3.6
1:3	0.5 mL seeds	0.05	1	4
2:1	0.5 mL seeds	0.05	3	2
3:1	0.5 mL seeds	0.05	3.5	1.5
1:1	0.5 mL seeds	0.05	2.1	2.8

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Characterization

For characterization, as prepared Au-ZnO particles were diluted in toluene and mixed by vigorous pipetting. UV-visible absorbance spectra were recorded using a HP-8453 spectrophotometer. The particles size and morphology were studied using

transmission electron microscopy (TEM). TEM images were obtained using a JEOL JEM-1230 TEM operating at 120 kV. Samples for TEM imaging were prepared by suspending a Formar carbon-coated, 300 mesh copper grid (Ted Pella) in toluene diluted samples for approximately 2 minutes. Particles were centrifuged from solution and powder X-ray diffraction (XRD) patterns of the particles were collected at room temperature using an X'Pert Philips Materials Research Diffractometer with $CuK_{\alpha}R$ radiation.

Table 2. Measured Temperatures following 10 min MWI (1000 W) with different ratios of OAc: OAm and total weight of recovered Au-ZnO nanocrystals.

Ratio OAc:OAm	Temp. after MWI 10 min. (°C)	Total weight* of recovered material (mg)
1:2	214	27
1:3	258	59
2:1	216	48
3:1	172	25
1:1	189	50

Table 3. Measured Temperatures following 10 min MWI using different powers with the 1:2 ratio of OAc: OAm and total weight of recovered Au-ZnO nanocrystals.

1:2 OAc:OAm Microwave power	Temp. after MWI 10 min. (°C)	Total weight* of recovered material (mg)
9	184	1
8	160	7
7	149	40
6	126	103
5	109	17

* For the total weight of material recovered, samples were centrifuged in previously weighed centrifuge tubes. After centrifugation, the samples were dried in at 60 °C overnight and weighed.

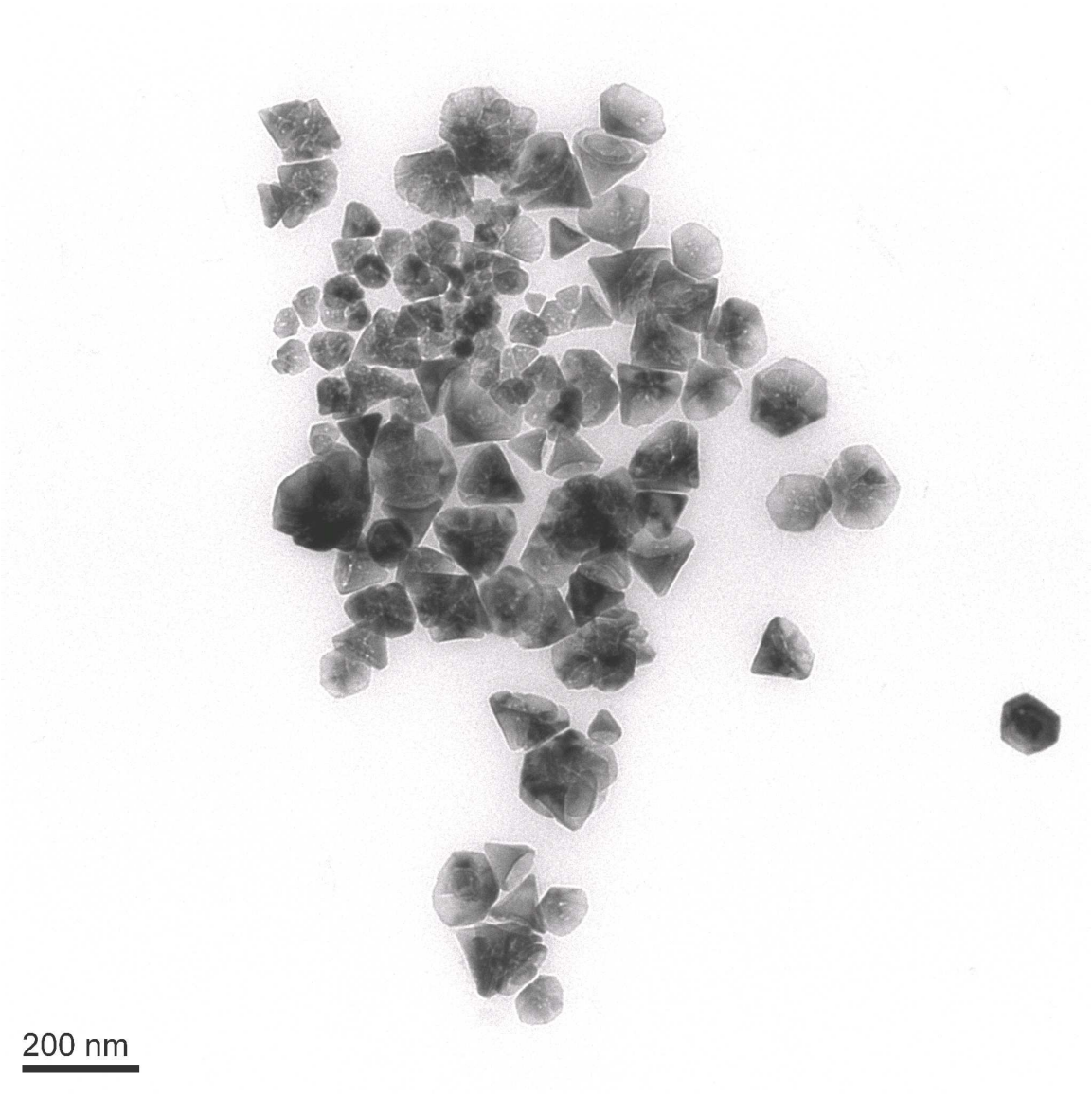

Figure S1. TEM image of ZnO nanopyramids prepared using 0.1 M zinc acetate in the presence of a 1:3 molar ratio of oleic acid to oleylamine obtained after 15 minutes MWI times (1000 W).

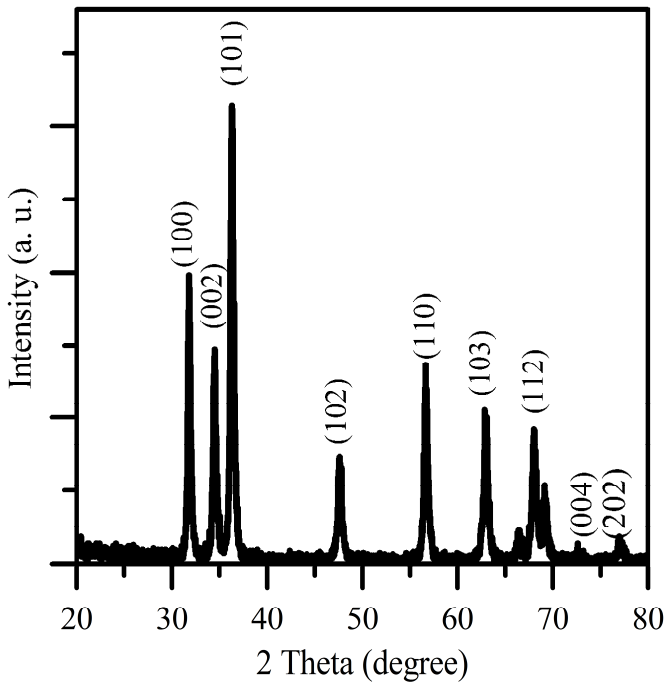

Figure S2. XRD for ZnO nanopyramids prepared from a mixture of 0.1 M zinc acetate in the presence of a 1:3 ratio of oleic acid : oleylamine after 15 minutes of microwave irradiation (1000 W).

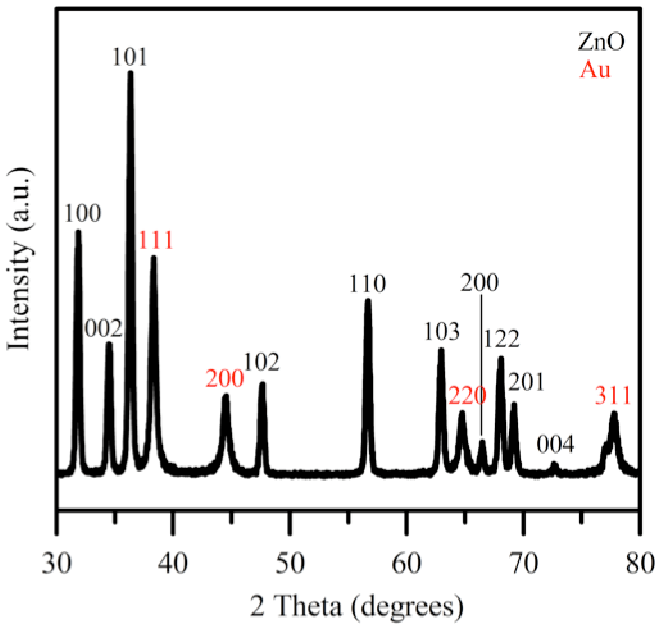

Figure S3. XRD for the Au-ZnO nanopyramids prepared using 0.17 M Zn acetate and 0.007 M $HAuCl_4$ in the presence of 1:1 molar ratio of oleic acid to oleylamine and 8 minutes MWI time (1000 W).

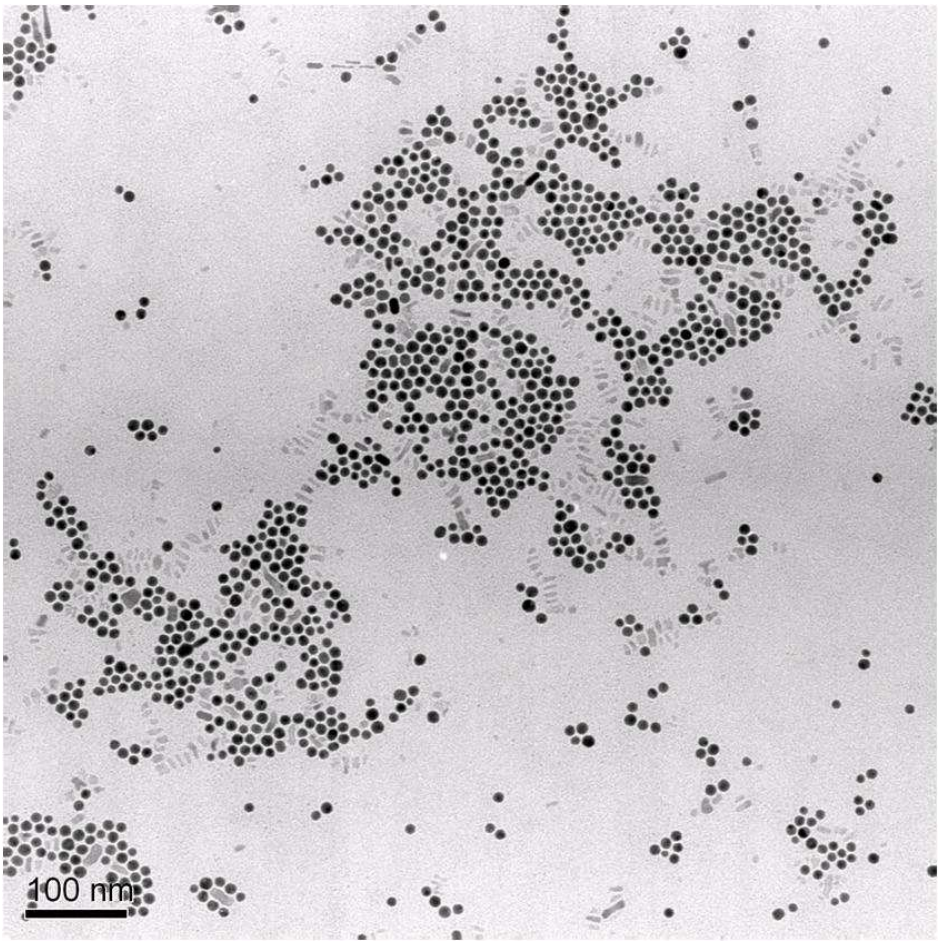

Figure S4. TEM image of nanoparticles (mostly Au nanoparticles) prepared using 0.17 M Zn acetate and 0.007 M $HAuCl_4$ in the presence of 1:1 molar ratio of oleic acid to oleylamine and one minute MWI time (1000 W).

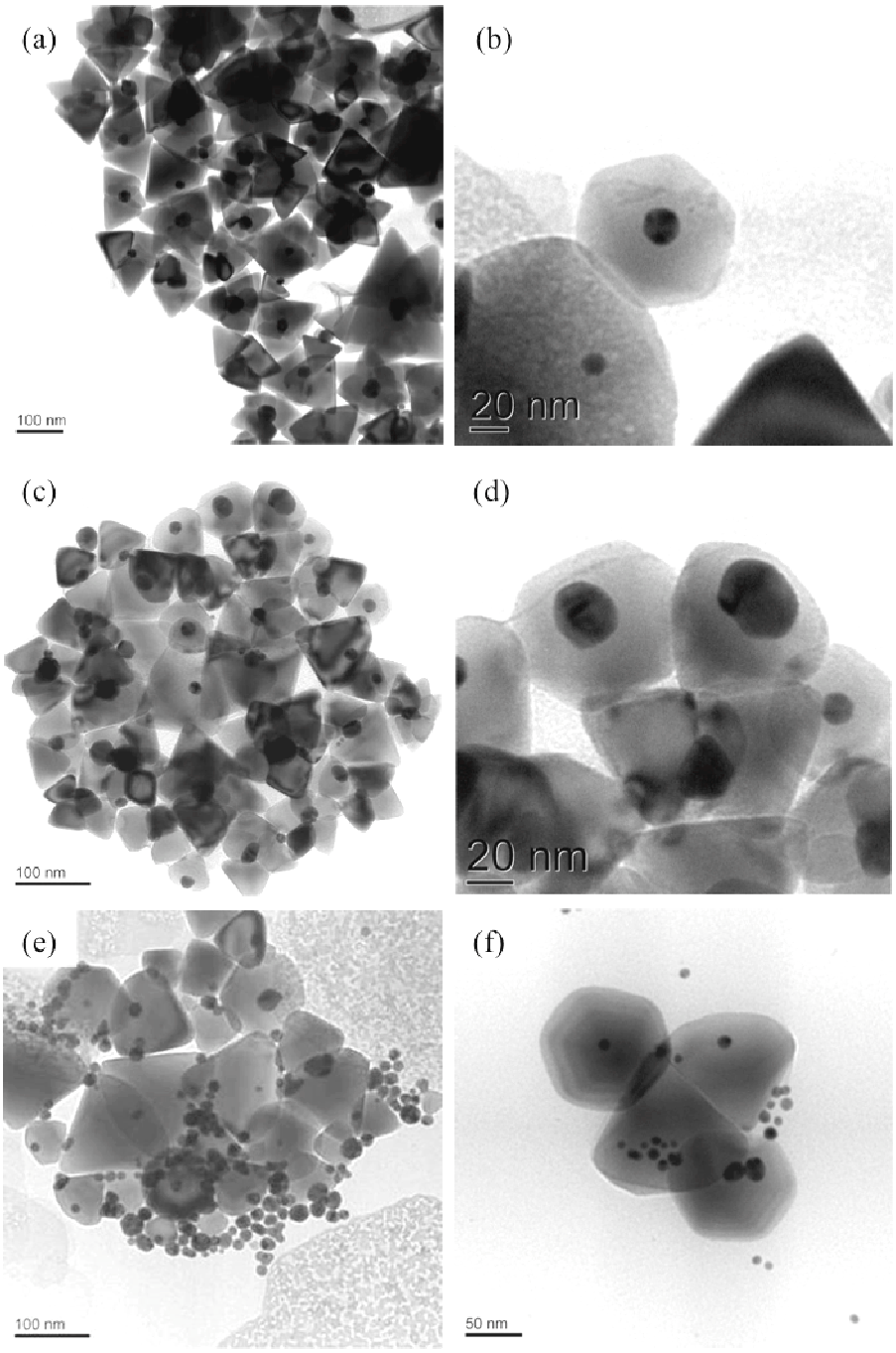

Figure S5. TEM images of Au-ZnO nanopyramids prepared using 0.17 M Zn acetate in the presence of 1:1 molar ratio of oleic acid to oleylamine and 8 minutes MWI time (1000 W) with different concentrations of $HAuCl_4$: (a-b) 0.004 M, (c-d) 0.007 M, (e) 0.014 M and (f) 0.014 M $HAuCl_4$, 12 min MWI time.

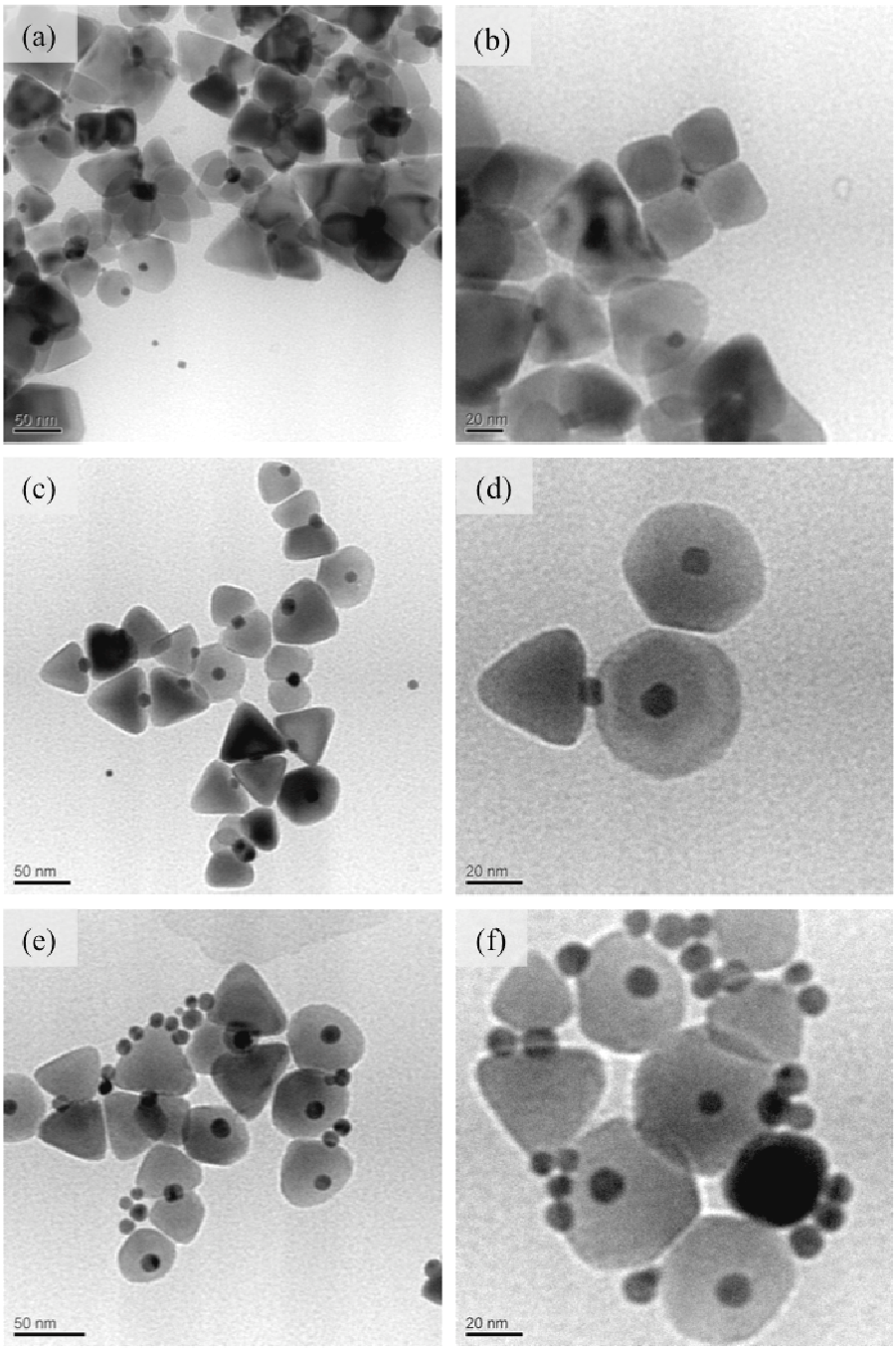

Figure S6. TEM images of Au-ZnO nanopyramids prepared using 0.25 M Zn acetate in the presence of 1:1 molar ratio of oleic acid to oleylamine (4 mL) and 10 minutes MWI time (1000 W) with different added volumes of preformed Au nanoparticles: (a-b) 0.5 mL, (c-d) 1 mL, (e-f) 2 mL.